

FORM PTO 1390 (REV 5-93) US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY DOCKET NUMBER 2001-1443A
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371		U.S. APPLICATION NO. (if known, see 35 U.S.C. §371) [NEW] 09/937724
International Application No. PCT/EPO0/02552	International Filing Date March 23, 2000	Priority Date Claimed April 13, 1999
Title of Invention SINGLET OXYGEN OXIDATION OF ORGANIC SUBSTRATES		
Applicant(s) For DO/EO/US Jean-Marie AUBRY, Veronique RATAJ-NARDELLO; Paul ALSTERS		
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. §371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. §371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. §371(c)(2)). ATTACHMENT A <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)). <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). ATTACHMENT B <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)). <p>Items 11. to 14. below concern other document(s) or information included:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. ATTACHMENT C <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <p>ATTACHMENT D</p> <ol style="list-style-type: none"> <input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <ol style="list-style-type: none"> <input checked="" type="checkbox"/> Other items or information: <ol style="list-style-type: none"> Cover Page of Published International Application No. WO 00/61524 - ATTACHMENT E International Search Report - ATTACHMENT F 		

U.S. APPLICATION NO. [NEW] 09/937724		INTERNATIONAL APPLICATION NO. PCT/EP00/02552	ATTORNEY'S DOCKET NO. 2001-1443A
15. [X] The following fees are submitted		CALCULATIONS	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International Search Report has been prepared by the EPO or JPO \$ 860.00 International preliminary examination fee not paid at USPTO but international search paid to USPTO \$ 710.00 International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 690.00 International preliminary examination fee paid at USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$ 100.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).			
Claims	Number Filed	Number Extra	Rate
Total Claims	8 -20 =	0	X \$18.00
Independent Claims	1 - 3 =	0	X \$80.00
Multiple dependent claim(s) (if applicable)		+ \$270.00	
TOTAL OF ABOVE CALCULATIONS =		\$860.00	
[] Small Entity Status is hereby asserted. Above fees are reduced by 1/2.			
SUBTOTAL =		\$860.00	
Processing fee of \$130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).		+	
TOTAL NATIONAL FEE =		\$860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40 per property		+ \$ 40.00	
TOTAL FEES ENCLOSED =		\$900.00	
		Amount to be refunded	\$
		Amount to be charged	\$
a. [X] A check in the amount of <u>\$ 900.00</u> to cover the above fees is enclosed. A duplicate copy of this form is enclosed. b. [] Please charge my Deposit Account No. 23-0975 in the amount of <u>\$ _____</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0975</u> .			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.			
19. CORRESPONDENCE ADDRESS		By: <u>Matthew Jacob</u> Matthew Jacob, Registration No. 25,154 WENDEROTH, LIND & PONACK, L.L.P. 2033 "K" Street, N.W., Suite 800 Washington, D.C. 20006-1021 Phone:(202) 721-8200 Fax:(202) 721-8250 September 28, 2001	
 000513 PATENT TRADEMARK OFFICE		THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY DEFICIENCY IN THE FEE FOR THIS PAPER TO DEPOSIT ACCOUNT NO. 23-0975.	
		[CHECK NO. <u>46728</u>] [2001-1443A]	

THE COMMISSIONER IS AUTHORIZED
 TO CHARGE ANY DEFICIENCY IN THE
 FEE FOR THIS PAPER TO DEPOSIT
 ACCOUNT NO. 23-0975.

Singlet oxygen oxidation of organic substances [sic]

The only singlet oxygen oxidation (${}^1\text{O}_2\text{-Ox}$) which is currently carried out industrially is the photochemical ${}^1\text{O}_2\text{-Ox}$ in which the ${}^1\text{O}_2$ is generated by a photochemical route. The disadvantage of this process is given by the high costs of the photochemical equipment required, and by a limited service life. The required lamps degenerate relatively rapidly during the oxidation as a result of soiling of the glass surface. In addition, this process is not suitable for colored substrates. The process is actually suitable only for fine chemicals which are prepared on a relatively small scale. (La Chimica e l'Industria, 1982, Vol. 64, page 156).

For this reason, attempts have been made to find other process variants for the ${}^1\text{O}_2\text{-Ox}$ which are suitable for the ${}^1\text{O}_2\text{-Ox}$ of non-water-soluble, hydrophobic organic substrates.

J. Am. Chem. Soc., 1968, 90, 975 describes, for example, the classical "dark" ${}^1\text{O}_2\text{-Ox}$ in which ${}^1\text{O}_2$ is not generated photochemically, but chemically. In this process, hydrophobic substrates are oxidized by means of a hypochlorite/ H_2O_2 system in a solvent mixture of water and organic solvent. However, this process has only found a few synthetic applications since many substrates are only sparingly soluble in the required medium. In addition, the use possibility is rather limited because of secondary reactions between hypochlorite and substrate or solvent. In addition, a large part of the ${}^1\text{O}_2$ is deactivated in the gas phase. In addition, this process is not suitable for industrial scale since in the organic medium addition of the hypochlorite onto H_2O_2 results, and a large excess of H_2O_2 is required to suppress the secondary reaction of substrate with hypochlorite. An additional disadvantage arises as a result of the formation of stoichiometric amounts of salt.

A variant of the "dark" ${}^1\text{O}_2\text{-O}_x$, which is not based on hypochlorite and thus should partly avoid the above disadvantages, is known, for example, from J. Org. Chem., 1989, 54, 726 or J. Mol. Cat., 1997, 117, 439, according to which some water-soluble organic substrates are oxidized with H_2O_2 and a molybdate catalyst in water as solvent. According to Membrane Lipid Oxid. Vol. II, 1991, 65, the ${}^1\text{O}_2\text{-O}_x$ of water-insoluble, organic substrates with the molybdate/ H_2O_2 system is difficult since it was assumed that none of the customary solvents is suitable for maintaining the disproportionation, catalyzed by molybdate, of H_2O_2 into water and ${}^1\text{O}_2$. As is described in Membrane Lipid Oxid. Vol. II, 1991, 65, water-insoluble substrates, such as, for example, α -terpinene or β -citronellol, can be oxidized with the molybdate/ H_2O_2 system in a MeOH/water mixture (70/30) with only relatively low yields of 70%. As well as the only moderate yields which are obtained using MeOH/water, the very small application spectrum of this method based on aqueous solvent mixtures is an additional disadvantage since this method, as is clear from J. Am. Chem. Soc., 1997, 119, 5286, is limited to somewhat hydrophilic substrates or to hydrophobic substrates with a low molecular weight.

J. Am. Chem. Soc., 1997, 119, 5286 and EP-A-0 288 337 describes a process that permits the generation, catalyzed by molybdate in aqueous solution, of ${}^1\text{O}_2$ from H_2O_2 and is nevertheless suitable for hydrophobic substrates from a relatively wide molecular weight range. In this process, a microemulsion is used as reaction medium. However, use on an industrial scale is associated with problems since product isolation from the microemulsion is difficult. In addition, it is a relatively expensive process since rather large amounts of surfactant have to be used relative to the substrate.

Accordingly, it was an object of the present invention to find an improved method of the "dark" $^1\text{O}_2$ -Ox which can be used simply, cost-effectively and in an environmentally friendly manner on an industrial scale 5 and is suitable for a large number of substrates.

Unexpectedly, it has now been found that the "dark" $^1\text{O}_2$ -Ox can be carried out in an extremely efficient manner with high yield in certain organic solvents as 10 reaction medium, without the addition of water as cosolvent and without surfactant.

Accordingly, the present invention provides a process for the oxidation of organic substrates by means of $^1\text{O}_2$, 15 which comprises adding 30-70% strength H_2O_2 to hydrophobic organic substrates which react with $^1\text{O}_2$ in an organic solvent in the presence of a heterogeneous or homogeneous catalyst, whereupon, following the catalytic decomposition of H_2O_2 to give water and $^1\text{O}_2$, 20 oxidation to give the corresponding oxidation products takes place.

The process according to the invention is suitable for the oxidation of hydrophobic organic substrates which 25 react with $^1\text{O}_2$.

Accordingly, substrates which may be used are the following compounds: olefins which contain one or more, i.e. up to 10, preferably up to 6, particularly preferably up to 4, C=C double bonds; electron-rich 30 aromatics, such as $\text{C}_6\text{-C}_{50}$, preferably up to C_{30} , particularly preferably up to C_{20} , phenols, polyalkylbenzenes, polyalkoxybenzenes; polycyclic aromatics having 2 to 10, preferably up to 6, particularly preferably up to 4 aromatic rings; 35 sulfides, such as, for example, alkyl sulfides, alkenyl sulfides, aryl sulfides which are either mono- or disubstituted on the sulfur atom, and heterocycles having an O, N or S atom in the ring, such as, for example, $\text{C}_4\text{-C}_{50}$, preferably up to C_{30} , particularly

preferably up to C₂₀, furans, C₄-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, pyrroles, C₄-C₆₀, preferably up to C₃₀, particularly preferably up to C₂₀, thiophenes. In this connection, the substrates may have
5 one or more substituents, such as halogen (F, Cl, Br, I), cyanide, carbonyl groups, hydroxyl groups, C₁-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, alkoxy groups, C₁-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, alkyl groups, C₆-C₅₀, preferably up
10 to C₃₀, particularly preferably up to C₂₀, aryl groups, C₂-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, alkenyl groups, C₂-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, alkynyl groups, carboxylic acid groups, ester groups, amide groups,
15 amino groups, nitro groups, silyl groups, silyloxy groups, sulfone groups, sulfoxide groups. In addition, the substrates may be substituted by one or more NR¹R² radicals in which R₁ [sic] or R₂ [sic] may be identical or different and are H; C₁-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, alkyl; formyl; C₂-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, acyl; C₇-C₅₀, preferably up to C₃₀, particularly preferably up to C₂₀, benzoyl, where R¹ and R² may also
20 together form a ring, such as, for example, in a phthalimido group.
25

Examples of suitable substrates are: 2-butene; isobutene; 2-methyl-1-butene; 2-hexene; 1,3-butadiene; 2,3-dimethylbutene; D^{9,10}-octalin [sic], 2-phthalimido-4-methyl-3-pentene; 2,3-dimethyl-1,3-butadiene; 30 2,4-hexadiene; 2-chloro-4-methyl-3-pentene; 2-bromo-4-methyl-3-pentene; 1-trimethylsilylcyclohexene; 2,3-dimethyl-2-butenyl-*para*-tolylsulfone; 2,3-dimethyl-2-butenyl-*para*-tolyl sulfoxide; N-cyclohexenylmorpholine; 2-methyl-2-norbornene; 35 terpinolene; α -pinene; β -pinene; β -citronellol; ocimene; citronellol; geraniol; farnesol; terpinene; limonene; *trans*-2,3-dimethylacrylic acid; α -terpinene; isoprene; cyclopentadiene; 1,4-diphenylbutadiene; 2-ethoxybutadiene;

1,1'-dicyclohexenyl; cholesterol; ergosterol acetate;
5-chloro-1,3-cyclohexadiene; 3-methyl-2-buten-1-ol;
3,5,5-trimethylcyclohex-2-en-1-ol; phenol,
1,2,4-trimethoxybenzene, 2,3,6-trimethylphenol,
5 2,4,6-trimethylphenol, 1,4-dimethylnaphthalene, furan,
furfuryl alcohol, furfural, 2,5-dimethylfuran,
isobenzofuran, dibenzyl sulfide, (2-methyl-5-*tert*-
butyl)phenyl sulfide etc.

10 As a result of the oxidation according to the invention, the corresponding oxidation product is obtained from the substrates. Alkenes, (polycyclic) aromatics or heteroaromatics give, in particular, hydroperoxides or peroxides which are able to further react under the reaction conditions to give alcohols, epoxides, acetals or carbonyl compounds, such as ketones, aldehydes, carboxylic acids or esters, if the hydroperoxide or the peroxide is unstable.

15 20 The oxidation according to the invention is carried out in an organic solvent.
Suitable solvents are C₁-C₈-alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol; ethylene glycol, propylene glycol, formamide,
25 N-methylformamide, dimethylformamide, sulfolane, propylene carbonate.
Preference is given to using methanol, ethanol, propanol, isopropanol, ethylene glycol, propylene glycol, formamide, N-methylformamide or
30 dimethylformamide, particularly preferably methanol, ethanol, ethylene glycol, propylene glycol, formamide or dimethylformamide as solvent.
Up to 25% of water may optionally be added to the organic solvent. However, the addition of water does
35 not bring any advantages for the reaction. Water is therefore preferably not added.

A metal which is suitable for ¹O₂ oxidations and is described, for example, in J. Am. Chem. Soc., 1985,

107, 5844 or in Membrane Lipid Oxid. Vol. II, 1991, 65, is added as heterogeneous or homogeneous inorganic catalyst to the solvent/substrate mixture.

5 In this connection, the metal can be in forms customary for ${}^1\text{O}_2$ oxidations, for example as the oxide, oxo complex, nitrate, carboxylate, hydroxide, carbonate, chloride, fluoride, sulfate, tetrafluoroborate, etc.

10 Preference is given to catalysts based on molybdenum, tungsten, scandium, vanadium, titanium, zirconium, praseodymium, neodymium, samarium, europium, terbium, dysprosium, holmium, erbium, ytterbium and lutetium. Particular preference is given to molybdenum catalysts.

15 The amount of catalyst used depends on the substrate used and is between 1 and 50 mol%, preferably between 5 and 25 mol%.

20 This is followed by the addition of 30-70% strength, preferably 40-60% strength, H_2O_2 . H_2O_2 is preferably added slowly or in portions to the reaction mixture of solvent, substrate and catalyst, the reaction mixture being stirred.

25 In the process according to the invention, the consumption of H_2O_2 is dependent on the substrate used. For reactive substrates, 2 to 3 equivalents of H_2O_2 are preferably needed, while less reactive substrates are preferably reacted with 3 to 10 equivalents of H_2O_2 .

30 The reaction temperature is between 0 and 50°C, preferably between 15 and 35°C.

35 In some cases, to improve activation of the catalyst, it may be advantageous to add customary basic or acidic additives to the reaction mixture.

The course of the reaction can be monitored by means of UV spectroscopy or by means of HPLC. When the reaction is complete, i.e. after 1 to 30 hours, depending on the

reaction conditions, the reaction mixture is worked up. Removal of the catalyst has proven unexpectedly simple particularly when molybdate catalysts are used, such as e.g. sodium molybdate, in some solvents. Although the 5 reaction proceeds completely homogeneously when molybdate catalysts, such as, for example, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in mono-hydroxylic, alcoholic solvents, i.e. in monohydric alcohols such as, for example, methanol or ethanol, are used, provided H_2O_2 is added, the catalyst, 10 after all of the H_2O_2 has been added, precipitates out of the reaction mixture, as a result of which the catalyst can be separated off by simple centrifugation or filtration, and recycled.

15 The end-product which remains can, where appropriate, be purified by means of recrystallization, extraction or distillation.

20 The process according to the invention permits the oxidation of a large number of hydrophobic compounds and is particularly advantageous for the oxidation of water-insoluble substrates which could not be oxidized with hitherto known chemical methods with high yield. Accordingly, the process according to the invention is 25 particularly suitable for the oxidation of unsaturated organic compounds, such as terpenes, for example α -terpinene and citronellol, aromatic polycycles, steroids, furans, cyclopentadienes, phenols etc., and generally for all compounds which react with $^1\text{O}_2$.

30 The process according to the invention gives the desired end-products in high yields of up to 100% with high purity.

35 The process according to the invention is characterized by the simple process regime which is best suited to the industrial scale since it can take place in simple multipurpose plants and with simple work-up steps, and can be used for a wide spectrum of substrates.

Example 1:

a) 0.2 ml of an aqueous 2 mol/l Na_2MoO_4 solution or
b) 0.4 mmol of $\text{Na}_2\text{MoO}_4 \cdot 2\text{eq}$.
5 were added to a thermostated solution (25°C) of 2 mmol of an organic substrate (α -terpinene or β -citronellol) in 4 ml of an organic solvent. 0.08 ml of H_2O_2 (50%) were added to this mixture. After the reaction mixture had turned yellow again, two further 0.08 ml portions 10 of H_2O_2 (50%) were added. The course of the reaction was monitored in the case of α -terpinene by means of UV spectroscopy (266 nm) and in the case of β -citronellol by means of HPLC (MeOH/ H_2O 70/30).

15 Example 2:

a) 0.2 ml of an aqueous 2 mol/l Na_2MoO_4 solution or
b) 0.4 mmol of $\text{Na}_2\text{MoO}_4 \cdot 2\text{eq}$.
were added to a thermostated solution (25°C) of 2 mmol 20 of an organic substrate (α -terpinene or β -citronellol) in 4 ml of an organic solvent. 0.25 ml of H_2O_2 (50%) were added to this mixture in one portion. The course 25 of the reaction was monitored in the case of α -terpinene by means of UV spectroscopy (266 nm) and in the case of β -citronellol by means of HPLC (MeOH/ H_2O 70/30).

The solvents used and the conversion of α -terpinene into ascaridol and β -citronellol into a 1/1 mixture of 30 the corresponding hydroperoxides are given in table 1:

Table 1:

Example	Substrate	Solvent	Cat. a) or b)	Conversion
1	α -terpinene	Methanol	a	100% after 2 h
1	α -terpinene	Methanol	b	>95% after 2 h
2	α -terpinene	Methanol	a	>95% after 2 h
1*	α -terpinene	Ethanol	a	90% after 22 h
1	α -terpinene	Formamide	a	70% after 21 h
1	α -terpinene	N-Me-formamide	a	75% after 3 h
1	α -terpinene	DMF	a	64% after 21 h
1	α -terpinene	Sulfolane	a	70% after 21 h
1	β -citronellol	Methanol	a	80% after 3 h
1	β -citronellol	Formamide	a	95% after 3 h

* 3rd portion of H_2O_2 was 0.09 ml

5

Example 3: Product isolation from reaction mixture with methanol as solvent

After the time given in table 1, the precipitated-out catalyst was removed from the reaction mixture by means of centrifugation. The precipitate was washed twice with absolute ethanol, and the combined solvent batches (methanol and ethanol) were removed on a rotary evaporator. The oxidation product which remained was dissolved in $CDCl_3$ for NMR analysis. In the case of α -terpinene, analysis confirmed the formation of a virtually quantitative amount of >95% pure ascaridol. In the case of β -citronellol, approximately 80% of product were obtained which, according to NMR analysis, consisted of a 1/1 mixture of the two corresponding hydroperoxides.

Example 4:

25 At 35°C, 45 μ l of H_2O_2 (50%) were added to a solution of 325 μ l of α -terpinene and 48.5 mg of $Na_2MoO_4 \cdot 2H_2O$ in 4 ml of methanol. Five further 45 μ l portions of H_2O_2

(50%) were added to this mixture as soon as the red-colored reaction mixture turned yellow again. After 1.5 hours, the reaction mixtures [sic] was analyzed by means of HPLC. Analysis gave a quantitative formation 5 of ascaridol.

Example 5.

At 25°C, 80 μ l of H_2O_2 (50%) were added to a solution of 10 365 μ l of citronellol and 97 mg of $Na_2MoO_4 \cdot 2H_2O$ in 4 ml of ethylene glycol. After 1, 2 and after 19 hours, 3 further 80 μ l portions of H_2O_2 (50%) were added to this mixture. HPLC analysis gave a 100% conversion with a 15 yield of secondary hydroperoxide of 38% and a yield of tertiary hydroperoxide of 62%.

Patent claims

1. A process for the oxidation of organic substrates by means of $^1\text{O}_2$, which comprises adding 30-70% strength H_2O_2 to hydrophobic organic substrates which react with $^1\text{O}_2$ in an organic solvent in the presence of a heterogeneous or homogeneous catalyst, whereupon, following the catalytic decomposition of H_2O_2 to give water and $^1\text{O}_2$, oxidation to give the corresponding oxidation products takes place.

5

2. The process as claimed in claim 1, wherein the substrates which react with $^1\text{O}_2$ used are olefins which contain 1 to 10 C=C double bonds; $\text{C}_6\text{-C}_{50}$ phenols, polyalkylbenzenes, polyalkoxybenzenes; polycyclic aromatics having 2 to 10 aromatic rings; alkyl sulfides, alkenyl sulfides, aryl sulfides which are either mono- or disubstituted on the sulfur atom, and $\text{C}_4\text{-C}_{60}$ heterocycles having an O, N or S atom in the ring, which may be unsubstituted or may be mono- or polysubstituted by halogens, cyanide, carbonyl groups, hydroxyl groups, $\text{C}_1\text{-C}_{50}$ alkoxy groups, 15 $\text{C}_1\text{-C}_{50}$ alkyl groups, $\text{C}_6\text{-C}_{50}$ aryl groups, $\text{C}_2\text{-C}_{50}$ alkenyl groups, $\text{C}_2\text{-C}_{50}$ alkynyl groups, carboxylic acid groups, ester groups, amide groups, amino groups, nitro groups, silyl groups, silyloxy groups, sulfone groups, sulfoxide groups 20 or by one or more NR^1R^2 radicals in which R_1 [sic] or R_2 [sic] may be identical or different and are H; $\text{C}_1\text{-C}_{50}$ alkyl; formyl; $\text{C}_2\text{-C}_{50}$ acyl; $\text{C}_7\text{-C}_{50}$ benzoyl, where R^1 and R^2 may also together form a ring.

25

3. The process as claimed in claim 1, wherein the solvent used is $\text{C}_1\text{-C}_8$ -alcohols, formamide, 30 N -methylformamide, dimethylformamide, sulfolane, propylene carbonate.

35

4. The process as claimed in claim 4, wherein the solvent used is methanol, ethanol, propanol, isopropanol, ethylene glycol, propylene glycol, formamide, N-methylformamide or dimethylformamide.

5

5. The process as claimed in claim 1, wherein catalysts based on molybdenum, tungsten, scandium, vanadium, titanium, zirconium, praseodymium, neodymium, samarium, europium, terbium, dysprosium, holmium, erbium, ytterbium or lutetium in the form of oxides, oxo complexes, nitrates, carboxylates, hydroxides, carbonates, chlorides, fluorides, sulfates or tetrafluoroborates are used.

15

6. The process as claimed in claim 1, wherein 2 to 10 equivalents of H_2O_2 are used depending on the substrate used.

20

7. The process as claimed in claim 1, wherein the reaction temperature is between 0 and 50°C.

25

8. The process as claimed in claim 1, wherein, following the reaction of the hydrophobic organic substrates which react with 1O_2 in a monohydric C_1-C_8 alcohol as solvent in the presence of a molybdate catalyst with 30-70% strength H_2O_2 to give the corresponding oxidation products, the removal and recycling of the precipitated-out catalyst when the reaction is complete is carried out by simple centrifugation or filtration.

30

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

Original Supplemental Substitute PCT Design

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: _____

of which is described and claimed in:

the attached specification, or
 the specification in the application Serial No. _____ filed _____;
 and with amendments through _____ (if applicable), or
 the specification in International Application No. PCT/ EP00/2552, filed 23/03/2000, and as amended
 on _____ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Austria	A 647 /99	13/04/1999	yes

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

22-1170-15

Full Name of Fifth Inventor	FAMILY NAME		FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY		STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS		CITY	STATE OR COUNTRY ZIP CODE
Full Name of Sixth Inventor	FAMILY NAME		FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY		STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS		CITY	STATE OR COUNTRY ZIP CODE
Full Name of Seventh Inventor	FAMILY NAME		FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY		STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS		CITY	STATE OR COUNTRY ZIP CODE

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor (Aubry Jean-Marie) *Jean* Date August 27, 2001
 2nd Inventor (Rataj-Nardelle Veronique) *Veronique* Date August 27, 2001
 3rd Inventor (Alsters Paul) *Paul* Date August 8, 2001
 4th Inventor _____ Date _____
 5th Inventor _____ Date _____
 6th Inventor _____ Date _____
 7th Inventor _____ Date _____

The above application may be more particularly identified as follows:

U.S. Application Serial No. _____ Filing Date _____
 Applicant Reference Number _____ Atty Docket No. _____
 Title of Invention _____

And I hereby appoint John T. Miller, Reg. No. 21,120; Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Jeffrey Nolton, Reg. No. 25,408; Warren M. Cheek, Jr., Reg. No. 33,367; Nils E. Pedersen, Reg. No. 33,145 and Charles R. Watts, Reg. No. 33,142, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., attorneys to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from Patent Department DSM Fine Chemicals Austria as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

Send Correspondence to

WENDEROTH, LIND & PONACK, L.L.P.
2033 K Street, N.W., Suite 800
Washington, DC 20006

Direct Telephone Calls to:

WENDEROTH, LIND & PONACK, L.L.P.
Area Code (202) 721-8200

Direct Facsimile Messages to:
Area Code (202) 721-8250

Full Name of First Inventor	FAMILY NAME <u>Aubry</u>	FIRST GIVEN NAME <u>Jean-Marie</u>	SECOND GIVEN NAME	
Residence & Citizenship	CITY <u>62590 Oignies</u>	STATE OR COUNTRY <u>France</u>	COUNTRY OF CITIZENSHIP <u>FR</u>	
Post Office Address	ADDRESS <u>13 Rue Casimir Beugnet</u>	CITY <u>62590 Oignies</u>	STATE OR COUNTRY <u>France</u>	ZIP CODE <u>FR</u>
Full Name of Second Inventor	FAMILY NAME <u>Rataj-Nardello</u>	FIRST GIVEN NAME <u>Veronique</u>	SECOND GIVEN NAME	
Residence & Citizenship	CITY <u>59650 Villeneuve d'Ascq</u>	STATE OR COUNTRY <u>France</u>	COUNTRY OF CITIZENSHIP <u>France</u>	
Post Office Address	ADDRESS <u>11/11 Place Cadet Rouselle</u>	CITY <u>59650 Villeneuve d'Ascq</u>	STATE OR COUNTRY <u>France</u>	ZIP CODE <u>FR</u>
Full Name of Third Inventor	FAMILY NAME <u>Alsters</u>	FIRST GIVEN NAME <u>Paul</u>	SECOND GIVEN NAME	
Residence & Citizenship	CITY <u>6224 KZ Maastricht</u>	STATE OR COUNTRY <u>The Netherlands</u>	COUNTRY OF CITIZENSHIP <u>The Netherlands</u>	
Post Office Address	ADDRESS <u>Oranjeplein 273</u>	CITY <u>6224 KZ Maastricht</u>	STATE OR COUNTRY <u>The Netherlands</u>	ZIP CODE <u>NL</u>
Full Name of Fourth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP	
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY	ZIP CODE